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16. ABSTRACT The article gives results of pilot plant tests to evaluate sodium thiosulfate as an oxidation inhibition additive in five lime/limestone slurry flue gas desulfurization processes. It was found th[at] the oxidation rate of absorbed SO2 was reduced by more than 50% in the presence [of] 00-200 ppm of thiosulfate ion in the scrubbing slurry. Calcium sulfate dihydr[ate] (gypsum) scaling was eliminated and the unsaturated (with respect to gypsum) op[eration] mode was maintained by the addition of sodium thiosulfate. Other benefits of soo[dium] thiosulfate addition observed at the pilot plant included improvement in solids dewatering properties for limestone processes and improvement in SO2 removal efficiency for magnesium-enhanced lime/limestone processes.

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Pilot Testing of Sodium Thiosulfate

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Pilot plant tests have been conducted to evaluate sodium thiosulfate as an oxidation inhibition additive in five lime/limestone slurry flue gas desulfurization processes. It was found that the oxidation rate of absorbed sulfur dioxide (SO_2) was reduced by more than 50 percent in the presence of 100 to 200 ppm of thiosulfate ion in the scrubbing slurry. Calcium sulfate dihydrate (gypsum) scaling was eliminated and the unsaturated (with respect to gypsum) operation mode was maintained by the addition of sodium thiosulfate. Other benefits of sodium thiosulfate addition observed at the pilot plant included improvement in solids dewatering properties for limestone processes and improvement in SO_2 removal efficiency for magnesium-enhanced lime/limestone processes.

INTRODUCTION

Due to the oxidation reaction between absorbed sulfur dioxide (SO_2) and dissolved oxygen, calcium sulfate dihydrate (gypsum) scaling in scrubber internals and associated equipment has been an operation and maintenance problem for lime/limestone slurry flue gas desulfurization (FGD) processes. A contributing factor to this problem is that older boilers tend to operate at higher levels of excess air. Scrubbers with induced-draft fans also have the potential of air leakage which enhances the oxidation.

Laboratory experiments have demonstrated that sodium thiosulfate is an effective oxidation inhibitor [*1*, 2]. It was reported that sodium thiosulfate, as an additive in the regenerable citrate FGD process, reduced the sulfur oxidation rate [3]. Pilot plant tests, conducted to evaluate the effectiveness of sodium thiosulfate in a limestone-regenerated dual alkali system, showed that sodium thiosulfate inhibits oxidation in the sodium sulfite/bisulfite clear-solution scrubber [*4*]. However, the effective level of thiosulfate needed to inhibit oxidation was proportional to the sulfite concentration. Therefore, large quantities of sodium thiosulfate would be needed for concentrated solution scrubbing processes.

The effects of thiosulfate on lime/limestone slurry processes are less consistent. The study of the retrofit scrubber system at Louisville Gas & Electric (LG&E) Paddy's Run Plant, which experienced little sulfate scaling, suggested that the presence of thiosulfate as an impurity in the carbide lime used might have inhibited oxidation and relieved gypsum scaling [*1*]. However, pilot plant tests, simulating this scrubber's operation by adding sodium thiosulfate to a conventional lime scrubber, did not show any oxidation reduction with thiosulfate addition [5]. The first successful application of commercial grade sodium thiosulfate to slurry FGD processes was at the Phillips Station of Duquesne Light which has a magnesium-enhanced lime system [6]. Gypsum scaling problems were caused by a combination of high excess air, low scrubber liquid-to-gas (L/G) ratio, low slurry solids content, and no hold tank to provide retention time for dissipating the sulfate saturation. The addition of sodium thiosulfate eliminated the scaling and substantially reduced maintenance requirements. In addition, a slight improvement of SO_2 removal was experienced. Noting this success, sodium thiosulfate was applied at Elrama Station, which also has a magnesium-enhanced lime scrubber, and similar benefits were obtained [6].

TVA Shawnee Station tested sodium thiosulfate in a prototype spray tower simulating limestone FGD processes [7]. Dramatic descaling effects were observed with the addition of sodium thiosulfate. Only 100 ppm of thiosulfate was needed to reduce the sulfate saturation and sustain scale-free operation. An unexpected benefit discovered was the improvement of solids dewatering properties as reflected by the increase of filter cake solids content. However, material balances showed that the sodium thiosulfate consumption was more than 10 times the estimated loss with filter cake moisture. Significant amounts of polythionates, ranging from dithionate to pentathionate, were found by chemical analyses of the scrubbing liquor [7].

Under the sponsorship of U.S. Environmental Protection Agency's (EPA) Industrial Environmental Research Laboratory (now Air and Energy Engineering Research

Laboratory, AEERL) at Research Triangle Park, NC, pilot plant tests were conducted to evaluate the effect of sodium thiosulfate as an additive to wet FGD systems. The objectives were to verify the oxidation reduction effect of sodium thiosulfate and to evaluate the effectiveness of thiosulfate in five lime/limestone slurry FGD processes. This paper summarizes the test results and compares them with previous data.

TEST FACILITIES

The test facility, located at EPA/AEERL's laboratories in Research Triangle Park, NC, is a three-stage mobile bed with 7.5-m³/min (approximately 0.1 MW) flue gas capacity (Figure 1). No flyash is present in the flue gas which is drawn from a gas-fired boiler and injected with pure SO_2. Typical operating conditions for the sodium thiosulfate evaluation tests are listed in Table 1. Adjustment of the lime or limestone slurry feed rate via feedback control was used to maintain constant hold tank pH.

High calcium limestone, quarried in Fredonia, Kentucky, and ground to 80% less than 325-mesh, was used as the reagent for the limestone tests. Hydrated lime, $Ca(OH)_2$, was mixed with water to make 30 wt.% solids slurries for the lime tests. Five FGD processes (limestone, lime, magnesium-enhanced lime, magnesium-enhanced limestone, and adipic-acid-enhanced limestone) were evaluated. In order to simulate magnesium-enhanced processes, epsom salt ($MgSO_4 \cdot 7H_2O$) was added to the hold tank to maintain the desired magnesium concentrations. Commercial grade adipic acid ($HOOC(CH_2)_4COOH$) was used for the organic-acid-enhanced limestone scrubber tests. Sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$) was the oxidation inhibition additive in all tests.

For each process, the pilot plant was first run without sodium thiosulfate to establish baseline performance. The scrubber slurry was then spiked with sodium thiosulfate to raise the thiosulfate concentration. Sodium thiosulfate was also added to the hold tank once per hour to replenish the losses and maintain constant thiosulfate concentration. The scrubber internals were inspected regularly to assess the extent of gypsum scaling. Slurry sulfate saturation level was obtained by liquid analyses and the Shawnee correlation: [7]

$$\% \text{ Sulfate saturation} = [Ca][SO_4] \left(\frac{26300}{3[Ca] + 3[Mg] + [SO_4]} + 4700 \right) \quad (1)$$

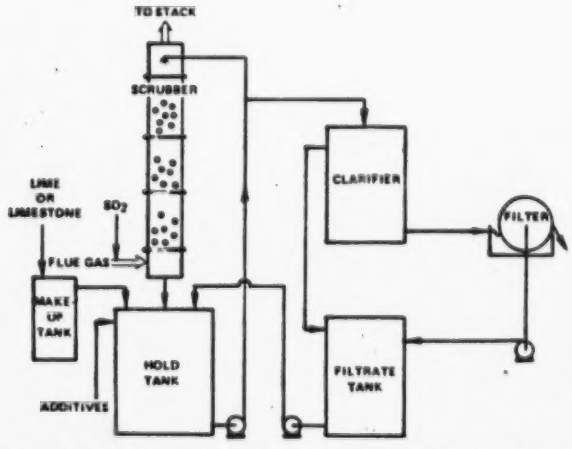

Figure 1. Flow diagram for thiosulfate tests in EPA/AEERL's 0.1 MW lime/limestone pilot plant system.

Table 1. Operating Conditions for Evaluation of Sodium Thiosulfate Additive at the AEERL Pilot Plant

Mobile bed absorber	= Three beds with 10-cm static bed height each
Packing	= 3.8-cm diameter nitrile foam spheres
L/G	= 4.7-8 l/m³ (35 to 60 gal./1000 acf) for lime and 9.3 l/m³ (70 gal./1000 acf) for limestone
Flue gas SO_2	= 2500-3000 ppm
Flue gas oxygen	= 7-8 vol. %
Hold tank solids	= 5-10 wt.%
Hold tank pH	= 6.5-7.5 for lime 5.5 for limestone
Hold tank residence time	= 2-5 minutes for lime 10 minutes for limestone

where [Ca], [SO_4], and [Mg] are total calcium, sulfate, and magnesium concentrations in moles/liter, respectively. The sulfate saturation, which is a good index of oxidation level and scaling potential, is defined as the quantity of dissolved calcium sulfate divided by its solubility concentration and expressed as a percentage. Oxidation level was measured by sulfite/sulfate analyses of filter cake samples. Ultraviolet spectrophotometry (DuPont 400 SO_2 analyzer) was used to monitor the gas-phase SO_2 concentrations and SO_2 removal efficiencies. Solids dewatering properties were characterized by hold tank slurry settling rates and filter cake insoluble solids concentrations.

The following analytical procedures were used for the analysis of sulfur species in the scrubbing liquor [6, 7]:

(1) Thiosulfate ($S_2O_3^{2-}$) by ion chromatography
(2) Total oxidizable sulfur (TOS) by oxidation with excess iodine and back titration with arsenous acid
(3) Sulfate (SO_4^{2-}) by ion chromatography
(4) Total sulfur by bromine oxidation and ion chromatography

Thiosulfate was also analyzed directly by formaldehyde fixation of sulfite/bisulfite followed by iodine oxidation and back titration of excess iodine with arsenous acid. Iodometric results agree reasonably well with ion chromatography results. The concentration of SO_3^{2-} plus HSO_3^- was estimated by the difference between results obtained from procedures (1) and (2). In addition to using procedure (4), total sulfur was also measured by H_2O_2/HCl oxidation and ion chromatography. However, bromine oxidation usually gave 10 to 20% more total sulfur than H_2O_2/HCl oxidation.

RESULTS AND DISCUSSION

As experienced in the TVA Shawnee tests [6], heavy doses of sodium thiosulfate were required initially to establish a sustainable sodium thiosulfate concentration. For example, in order to obtain a sustainable sodium thiosulfate concentration of 300 ppm, dosages sufficient to attain 2000 ppm sodium thiosulfate were used to spike the hold tank slurry at the beginning of the run. Usually, more than 80% of the spiked sodium thiosulfate disappeared within the first 24 hours, leaving only 200 to 300 ppm thiosulfate ions.

Results of pilot plant tests with and without sodium thiosulfate addition are summarized in Tables 2 to 7 for the five lime/limestone flue gas desulfurization processes tested. Table 2 shows that sodium thiosulfate addition effectively reduced oxidation, gypsum scaling, and sulfate saturation for all five FGD processes. The oxidation reduction is reflected by the significant drops of calcium and sulfate ion concentrations and by the observation that gypsum scaling disappeared after sodium thiosulfate addition (Tables 3 to 7). The unsaturated mode of operation (sulfate

TABLE 2. EFFECTS OF SODIUM THIOSULFATE ADDITION ON THE PERFORMANCE OF LIME/LIMESTONE SLURRY FGD SYSTEMS

Process Effect	Gypsum Scaling Abatement	Oxidation Reduction	Sulfate Saturation Reduction	SO_2 Removal Enhancement	Improved Solids Dewatering Properties
Limestone slurry	Yes	Yes	Yes		Yes
Lime slurry	Yes	Yes	Yes		
Magnesium-enhanced lime	Yes	Yes	Yes	slight	
Magnesium-enhanced limestone	Yes	Yes	Yes	Yes	
Adipic-acid-enhanced limestone	Yes	Yes	Yes	Yes	Yes

TABLE 3. SUMMARY OF LIMESTONE THIOSULFATE TEST RESULTS

Run No.	LS-0	LS-1	LS-2	LS-3	LS-4	LS-5
S_2O_3 level, ppm	0	100	500	1020	2250	1000
Gypsum scaling	Yes	No	No	No	No	No
Oxidation, %	20.6	—	6.1	5.1	1.2	1.3
Sulfate saturation, %	139.0	53.0	18.3	15.7	10.7	<2.3
Hold tank slurry settling rate, c/min	0.7	0.7	0.8	0.9	2.6	3.6
Filter cake solids, %	56	55	55	54	65	75
SO_2 removal, %	78	78	80	79	80	79
Limestone utilization, %	85	86	92	97	96	85
Ca, ppm	1000	520	270	250	250	1410
SO_4, ppm	2800	1450	790	660	370	<50
TOS[a] as SO_3, ppm	1100	—	2700	3100	3650	1320
TS[b] as SO_4, ppm	4100	—	5640	7300	9730	2980
Other sulfur as SO_4, ppm	0	—	750	1200	1120	160
Na, ppm	90	—	550	850	1350	760
Mg, ppm	300	360	420	380	450	890
Cl, ppm	<100	—	<100	<100	<100	3000
$Na_2S_2O_3$ makeup, gmole/hr	0	—	0.06	0.13	0.25	0.03
SO_2 oxidized, gmole/hr	4.7	—	1.4	1.2	0.28	0.30
Thiosulfate consumption, mmole $Na_2S_2O_3$ added/mole SO_2 absorbed	0	—	2.6	5.5	10.7	1.3
Test period, hrs	82	28	92	82	87	96

[a] TOS = total oxidizable sulfur
[b] TS = total sulfur

TABLE 4. SUMMARY OF LIME THIOSULFATE TEST RESULTS

Run No.	L-0	L-1	L-2	L-3	L-4
S_2O_3 level, ppm	0	100	300	500	2000
Gypsum scaling	Yes	No	No	No	No
Oxidation, %	20.0	—	10.8	8.8	4.7
Sulfate saturation, %	144.0	96.8	82.8	57.3	22.4
Hold tank slurry settling rate, cm/min	0.4	0.3	0.3	0.4	0.4
Filter cake solids, %	52	52	53	52	53
SO_2 removal, %	66	66	66	66	67
Lime utilization, %	99	—	97	99	98
Ca, ppm	992	724	620	510	207
SO_4, ppm	3080	2540	2480	1970	1460
TOS as SO_3, ppm	1080	—	—	—	960
TS as SO_4, ppm	4380	—	6420	6670	9920
Other sulfur as SO_4, ppm	0	—	—	—	3880
Na, ppm	120	520	720	1020	1860
Mg, ppm	350	420	460	510	510
Cl, ppm	160	—	250	200	210
$Na_2S_2O_3$ makeup, gmole/hr	0	—	0.06	0.13	0.32
SO_2 oxidized, gmole/hr	5.9	—	3.13	2.6	1.4
Thiosulfate consumption, mmole $Na_2S_2O_3$ added/mole SO_2 absorbed	0	—	2.07	4.4	10.7
Test period, hrs	78	38	82	86	82

saturation less than 100 percent) was sustained for all runs in the presence of thiosulfate ions.

Correlations between thiosulfate ion concentration and sulfate saturation/calcium ion concentration of the limestone slurry process were developed from the TVA/Shawnee spray tower test results. Comparisons of current data with the Shawnee correlations are shown in Figures 2 and 3. These show that the effects of thiosulfate on sulfate sat-

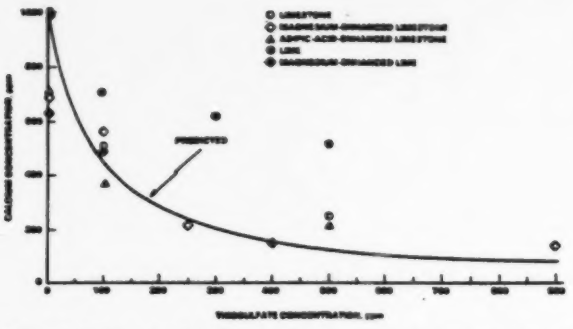

Figure 2. Predicted and measured calcium concentration as a function of thiosulfate concentration.

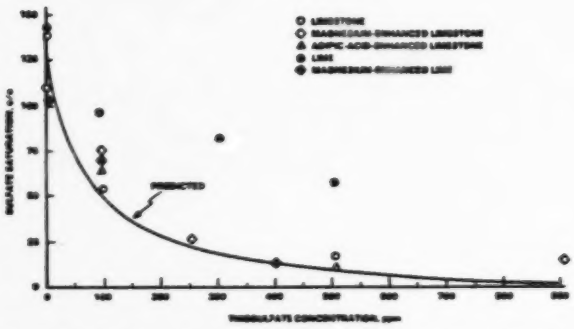

Figure 3. Predicted and measured sulfate saturation as a function of thiosulfate concentration.

uration and calcium ion concentration observed at the RTP pilot plant agree with the Shawnee results for all limestone tests. For the lime processes, the effects of thiosulfate concentration were less than predicted. However, for both cases, only 100 to 200 ppm thiosulfate ions were needed to significantly reduce the sulfite oxidation and avoid gypsum scaling.

Three possible inhibition mechanisms have been proposed by Miller *et al.* [6] to explain the oxidation reduction effects of thiosulfate. The first mechanism postulates that the overall oxidation can be reduced by the formation of an unoxidizable compound between sulfite and thiosulfate or by selective oxidation of thiosulfate rather than sulfite. Current data do not support these mechanisms because the thiosulfate required would be equal to the amount of sulfite normally oxidized in its absence. The results in Tables 3 through 7 indicate that the thiosulfate consumption rate is at least an order of magnitude less than the sulfite oxidation rate. Table 4 and 5 show that even with lime processes, for which thiosulfate addition is less effective, 0.06 gmole/hr of thiosulfate reduces sulfite oxidation by more than 2.5 gmole/hr, thus totally invalidating the selective oxidation mechanism.

It has been recognized that the sulfite is usually oxidized via a series of free radical chain reactions [8] which are initiated/catalyzed by several metal ions even at trace levels. Therefore, the second possible oxidation inhibition mechanism is that metal-thiosulfate complexes, which interrupt the chain reactions and reduce sulfite oxidation, are formed in the lime/limestone slurries. Selected values for several metals considered to be oxidation catalysts are given in Table 8 [9]. The metal-thiosulfate equilibrium constant, K, was used to calculate the residual concentration of metal ion in solution, assuming a metal ion concentration of 50 ppm and thiosulfate ion concentration of 250 ppm prior to complexing. The calculations show that the concentrations of transition metals, such as Mn^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+}, are not significantly affected by the presence of thiosulfate ion. On the other hand, substantial concentration reductions are possible if Fe^{3+} is present. Heavy metal ions such as Cu^{+} and Cu^{2+} can even be eliminated by the addition of thiosulfate. Thus, oxidation inhibition by complexing the catalysts with thiosulfate is possible, especially when the oxidation reaction is catalyzed by metals ions such as Fe^{3+}, Cu^{+}, and Cu^{2+}.

Metal-thiosulfate complexing mechanisms cannot fully explain the oxidation inhibition observed in the pilot plant tests. First, the metal ion concentrations in RTP pilot plant scrubbing liquor are normally less than 50 ppm. Therefore, less than 200 ppm sodium thiosulfate is needed to form the metal-thiosulfate complex. However, current test results and TVA/Shawnee data indicated that the system had to be initially spiked with sodium thiosulfate sufficient for 2000 ppm. Second, previous pilot dual alkali data [4] showed that the thiosulfate level required for effective oxidation reduction is proportional to sulfite concentration. Therefore, in addition to metal-thiosulfate complexing, another (the third) mechanism involving sulfite ions is postulated.

The third possible mechanism is based on the assumption that, with free radical chain reactions, the oxidation of sulfite can also be slowed by reaction of thiosulfate with a chain-sustaining radical (e.g., $\cdot SO_3^-$) to form a nonreactive stable compound. The concentration, or generation rate, of the free radicals is very likely a function of sulfite concentration; thus, the effective oxidation reduction concentration of thiosulfate as indicated by dual alkali testing. Current data also show that there are always "unknown sulfur species" in the scrubbing slurry with thiosulfate addition. Chemical analyses of the Shawnee spray tower samples found significant amounts of polythionates (up to pentathionate) which are the typical products of thiosulfate-radical reactions [10]. If the oxidation is inhibited by free-radical scavenging of thiosulfate, current testing indicated that significant amounts of sodium thiosulfate are needed for initial quenching of chain reactions and establishing a sustainable thiosulfate level.

The sodium thiosulfate makeup rates shown in Tables 3 to 7 are the average $Na_2S_2O_3 \cdot 5H_2O$ feed rates after the initial spikes for each run. The makeup rate includes sodium thiosulfate required to replenish the loss with scrubbing liquor contained in filter cake and the thiosulfate consumed (degraded) by reaction with metal ions or free radicals. For purposes of scale-up and material balance, the sodium thiosulfate consumption rate was normalized against SO_2 absorption rate. The pilot test data shown in Tables 3 to 7 indicate that the normal thiosulfate consumption rate for oxidation/scaling inhibition should be in the range of 1 to 3 mmole $Na_2S_2O_3$ added/mole SO_2 absorbed for both the lime and limestone slurry FGD systems.

Results specific to each process tested are discussed in the following sections.

Limestone Slurry Process

Four runs were made with sodium thiosulfate concentrations ranging from 100 to 2250 ppm [Table 3]. In addition to decreases in oxidation and sulfate saturation, the most significant effect observed with thiosulfate additive was improved solids qualities (Tables 2 and 3). When the thiosulfate ion concentration was increased to 2250 ppm (run LS-4), the bold tank slurry settling rate also increased to 2.6 cm/min (vs. 0.7 cm/min for the base case, run LS-0) and filter cake insoluble solids reached 65% (vs. 56% for the base case). The slurry settling rate was taken as average descending rate of the meniscus in a 100-ml graduated cylinder over the first 2 minutes as shown in Figure 4. Although a Coulter Counter analysis did not show a

Table 5. Summary of Magnesium-Enhanced Lime Test Results

Run No.	LM-0	LM-1	LM-2	LM-3
S_2O_3 level, ppm	0	100	400	3000
Gypsum scaling	Light	No	No	No
Oxidation, %	17.0	—	10.0	5.2
Sulfate saturation, %	102	70.3	18.4	0.76
Hold tank slurry settling rate, cm/min	0.3	0.3	0.3	0.3
Filter cake solids, %	43	43	43	42
SO_2 removal, %	95	95	97	98
Lime utilization, %	97	—	98	99
Ca, ppm	630	490	260	40
SO_4, ppm	8550	7120	2780	690
TOS as SO_3, ppm	1040	—	1680	—
TS as SO_4, ppm	9800	—	8760	13200
Other sulfur as SO_4, ppm	0	—	3280	—
Na, ppm	30	—	480	1840
Mg, ppm	2020	2010	2030	2010
Cl, ppm	30	—	40	40
$Na_2S_2O_3$ makeup, gmole/hr	0	—	0.06	0.38
SO_2 oxidized, gmole/hr	6.2	—	3.7	1.9
Thiosulfate consumption, mmole $Na_2S_2O_3$ added/mole SO_2 absorbed	0	—	1.6	10.4
Test period, hrs	68	32	76	85

Table 6. Summary of Magnesium-Enhanced Limestone Test Results

Run No.	LSM-0	LSM-1	LSM-2	LSM-3	LSM-4
S_2O_3 level, ppm	0	100	250	900	7000
Gypsum scaling	light	No	No	No	No
Oxidation, %	19.2	—	8.3	4.1	—
Sulfate saturation, %	110.3	75.3	26.9	17.9	7.0
Hold tank slurry settling rate, cm/min	0.7	0.7	0.8	0.7	1.0
Filter cake solids, %	54	54	54	54	56
SO_2 removal, %	83	83	85	88	—
Lime utilization, %	92	92	93	94	93
Ca, ppm	701	562	221	170	140
SO_4, ppm	5960	4620	3660	3020	1500
TOS as SO_3, ppm	1625	—	2810	4010	4670
TS as SO_4, ppm	7810	—	7820	—	19400
Other sulfur as SO_4, ppm	0	—	360	—	296
Na, ppm	90	—	364	812	3500
Mg, ppm	1250	1250	1270	1240	1250
Cl, ppm	90	—	90	80	80
$Na_2S_2O_3$ makeup, gmole/hr	0	—	0.04	0.12	—
SO_2 oxidized, gmole/hr	4.5	—	2.0	1.0	—
Thiosulfate consumption, mmole $Na_2S_2O_3$ added/mole SO_2 absorbed	0	—	1.7	4.5	—
Test period, hrs	68	36	76	83	81

significant difference in the hold tank slurry particle size distributions between runs LS-0 and LS-4 (Figure 5), scanning electron micrographs (Figures 6 and 7) indicate that the platelet-like solid particles obtained with a 2250 ppm thiosulfate concentration are generally larger and have fewer defects than those obtained without sodium thiosulfate addition.

Significant solids quality improvement was also noted in TVA/Shawnee spray tower testing with sodium thiosulfate addition. However, the effects observed at the RTP pilot plant differ from the TVA/Shawnee findings in three respects: (1) no changes in solids qualities were obtained until the thiosulfate concentration reached 2000 ppm at RTP, whereas the TVA/Shawnee tests showed a significant increase in filter cake solids at thiosulfate ion concentrations as low as 500 ppm; (2) the oxidation was usually below 5% when solids quality changed at RTP, as contrasted with improvements in solids quality at TVA/Shawnee with oxidation as high as 15%; and (3) at RTP, increases in filter cake insoluble solids were always accompanied by higher settling rate, but only filter cake solids increases were reported by TVA/Shawnee testing.

Interesting results were derived from a run (LS-5) made with calcium chloride added to the hold tank to raise the chloride ion concentration to 3000 ppm while maintaining a 1000 ppm thiosulfate concentration (Table 3). An oxidation of 1.3% was obtained with sulfate saturation less than 2.3%. The hold tank slurry settling rate was 3.6 cm/min, and filter cake insoluble solids reached 75%. A Coulter Counter analysis indicated that the mean particle size was considerably larger than those from runs without calcium chloride addition (Figure 5). Scanning electron micrographs (Figure 8) also reveal significant changes in crystal morphology. Thick, bulky crystals (instead of thin platelets) were obtained after the calcium chloride addition. The results suggest a synergistic effect of $CaCl_2$ on thiosulfate in terms of both oxidation reduction and solids quality improvement.

TABLE 7. SUMMARY OF ADIPIC-ACID-ENHANCED LIMESTONE TEST RESULTS

Run No.	LA-0	LA-1	LA-2	LA-3	LA-4
S_2O_3 level, ppm	0	100	500	2200	2000
Gypsum scaling	Light	No	No	No	No
Oxidation, %	17	—	5.3	2.9	0.9
Sulfate saturation, %	185.8	64.1	10.6	4.3	4.0
Hold tank slurry settling rate, cm/min	—	1.2	1.2	1.8	4.0
Filter cake solids, %	48	49	52	59	69
SO_2 removal, %	88	89	93	95	96
Lime utilization, %	95	—	90	91	93
Ca, ppm	710	372	220	180	530
SO_4, ppm	9270	4820	1250	610	220
TOS as SO_3, ppm	3580	—	2890	4450	3660
TS as SO_4, ppm	—	—	6220	—	8920
Other sulfur as SO_4, ppm	—	—	640	—	540
Na, ppm	6650	—	4220	5060	5230
Mg, ppm	830	962	1230	1270	1320
Cl, ppm	5610	—	6040	5810	7490
$Na_2S_2O_3$ makeup, gmole/hr	0	—	0.06	0.29	—
SO_2 oxidized, gmole/hr	6.7	—	2.02	1.192	0.38
Adipic acid makeup, g/hr	25	—	25	25	25
Thiosulfate consumption, mmole $Na_2S_2O_3$ added/mole SO_2 absorbed	0	—	1.6	7.6	—
Test period, hrs	258	38	248	72	78

Lime Slurry Process

Pilot plant tests were conducted in 1978 to evaluate sodium thiosulfate additive as an oxidation inhibitor in lime FGD systems [5]. No significant differences in overall oxidation were obtained between runs with and without thiosulfate. It was concluded that sodium thiosulfate was not an effective oxidation inhibitor in the lime scrubber.

Four pilot tests were conducted during the current test series to further investigate the oxidation inhibition effect of sodium thiosulfate in the lime scrubber (Table 4). One run (L-0) was made without sodium thiosulfate to provide a basis for comparing the effect of the additive on oxidation. The system was operated saturated with respect to sulfate (116% sulfate saturation in the hold tank). Filter cake analyses show that 20% oxidation was obtained, which is very close to the 23% attained during the 1978 tests [5]. Substantial decreases of calcium and sulfate ion concentrations in scrubbing liquor were obtained following the addition of sodium thiosulfate (runs L-1, L-2, and L-3). The system was operated unsaturated with respect to sulfate with thiosulfate addition, although no improvement of solids dewatering properties was obtained at 2000 ppm thiosulfate. Solid analyses also showed that oxidation was significantly reduced. Therefore, based on the results of current testing, it is apparent that sodium thiosulfate is an effective oxidation inhibitor in lime scrubbers.

To explain the discrepancy between the 1978 data [5] and current results, operating conditions and test procedures were compared. The main differences are the flue gas compositions and the scrubbing liquor chloride ion concentrations. The scrubber inlet flue gas contained no HCl, and the scrubbing liquor chloride ion concentration

TABLE 8. EQUILIBRIUM CONSTANTS OF METAL-THIOSULFATE COMPLEXES

Metal ion	i[a]	K[b]	Metal ion complexed, %[c]
Mn^{2+}	1	89	15.6
Fe^{2+}	1	148	23.1
Fe^{3+}	1	447	45.0
Co^{2+}	1	112	18.6
Ni^{2+}	1	115	18.9
Cu^{+}	3	10^{13}	>99
Cu^{2+}	2	10^{13}	>99

[a] i = number of thiosulfate ions assumed complexed with the metal ion
[b] K = metal-thiosulfate complex equilibrium constant = [complex]/([metal ion][thiosulfate]^i)
[c] 50 ppm metal ion and 250 ppm thiosulfate ion concentrations prior to complexing

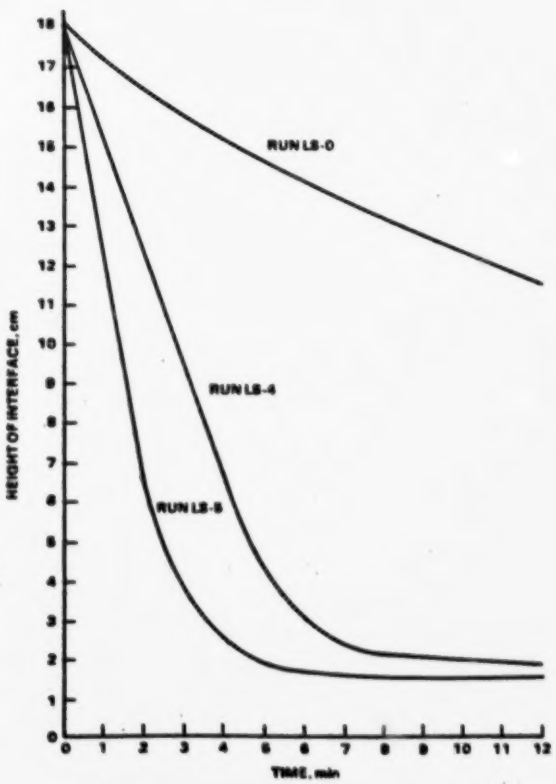

Figure 4. Settling curves for runs LS-0, LS-4, and LS-5.

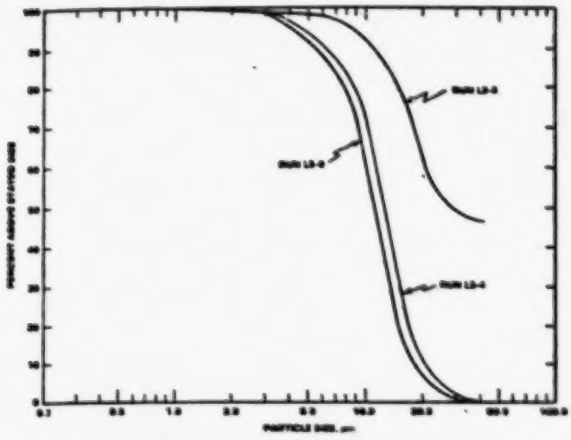

Figure 5. Results of coulter counter particle size analysis.

was below 300 ppm for current tests. However, during the 1978 tests, chloride was fed as HCl gas into the scrubber inlet duct, and the scrubbing liquor chloride ion concentration reached as high as 14,700 ppm. The data showed a strong correlation between the oxidation and the chloride ion concentration, regardless of whether thiosulfate was present or not. It is very likely that the effect of chloride on oxidation was greater than the effects of thiosulfate addition under the operating conditions of 1978 tests. In view of the fact that no high chloride runs were made during the current testing, it is concluded that sodium thiosulfate is an effective oxidation inhibitor in lime scrubbers when the scrubbing liquor chloride ion concentration is below 300 ppm. When the HCl in flue gas causes high chloride ion concentrations, thiosulfate could be less effective.

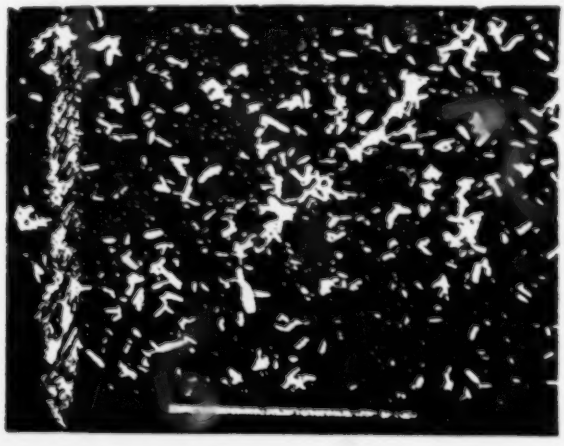

Figure 6. Scanning electron micrographs of solid products from limestone thiosulfate base case test (run LS-0, no thiosulfate addition). (a) Base case; 50x. (b) Base case; 500x.

Figure 7. Scanning electron micrographs of solid products from limestone thiosulfate test with 2250 ppm thiosulfate (run LS-4). (a) 2250 ppm thiosulfate; 50x. (b) 2250 ppm thiosulfate; 200x.

Magnesium-Enhanced Lime/Limestone Slurry Processes

The SO_2 scrubbing capacity of lime/limestone slurry can be enhanced by increasing total magnesium. Magnesium acts to promote high concentrations of the ion pairs, $MgSO_4^\circ$ and $MgSO_3^\circ$, with the magnesium sulfite ion pair reacting with dissolved SO_2 to enhance SO_2 removal. Cronkright and Leddy [11] suggested that the ion pair equilibrium relationship can be expressed as:

$$\frac{[MgSO_3^\circ]}{[MgSO_4^\circ]} = \frac{\gamma_{CaSO_3}}{\gamma_{CaSO_4}} \times C = R \qquad (2)$$

where γ is the saturation level and C is a constant. If the calcium sulfate saturation, γ_{CaSO_4}, is substantially reduced by sodium thiosulfate addition and the sulfite saturation remained relatively constant, Equation (2) indicates that the value of R should increase substantially. Furthermore, Equation (2) also indicates that, when the total magnesium is constant, the $MgSO_3^\circ$ concentration, and thus SO_2 scrubbing capacity, should increase with R. Therefore, ad-

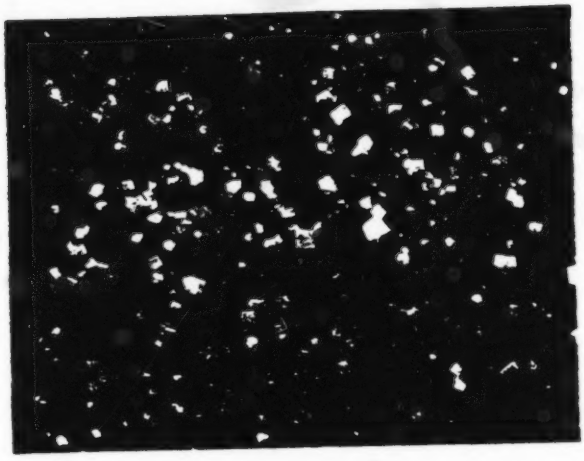

Figure 8. Scanning electron micrographs of solid products from limestone thiosulfate tests with 3000 ppm chloride and 1000 ppm thiosulfate (run LS-5). (a) 3000 ppm chloride, 1000 ppm thiosulfate; 50x. (b) 3000 ppm chloride, 1000 ppm thiosulfate; 200x.

dition of sodium thiosulfate to magnesium-enhanced lime/limestone scrubbers could result in greater SO_2 removal.

It is difficult to estimate the ion pair concentrations; however, they can be related to other measurable quantities. At constant pH and total magnesium, the ratio of magnesium ion pairs should be proportional to the ratio of total sulfite to sulfate:

$$\frac{[MgSO_3^\circ]}{[MgSO_4^\circ]} = C' \frac{[SO_3]_T}{[SO_4]} \qquad (3)$$

where C' is a proportionality constant. Combining Equations (2) and (3) and using data without sodium thiosulfate addition as the base case (labeled by subscript B), the following relationship is obtained:

$$\frac{([SO_3]_T/[SO_4])}{([SO_3]_T/[SO_4])_B} = \frac{(\gamma_{CaSO_4})_B}{(\gamma_{CaSO_4})} \qquad (4)$$

Figure 9 shows the comparisons between pilot plant data and Equation (4). The deviation could be caused by factors such as sulfite and sulfate activity coefficients and the variation in sulfite saturation levels not included in Equation (4).

The increase of SO_2 removal efficiency with sodium thiosulfate addition was also verified by pilot plant testing.

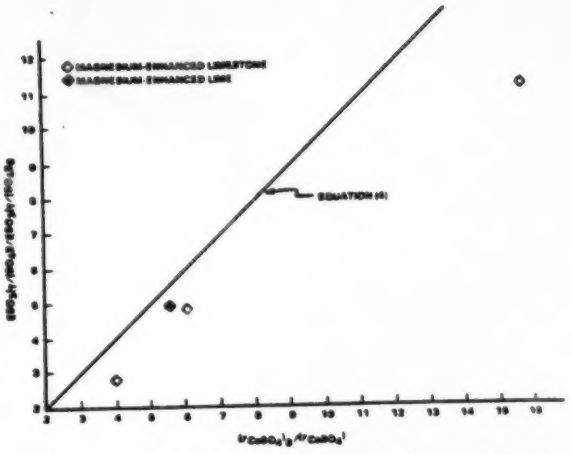

Figure 9. Comparison of pilot plant data with prediction curve of Equation (4).

Table 6 shows that, for the magnesium-enhanced limestone scrubbing, SO_2 removal efficiency increased from 83% to 85% by adding 250 ppm thiosulfate. A further increase of SO_2 removal to 88% was obtained at 900 ppm thiosulfate. Slight increases in SO_2 removal were also obtained with the magnesium-enhanced lime scrubber as shown in Table 5.

Adipic-Acid-Enhanced Limestone Slurry Process

In addition to oxidation inhibition, the purpose of this testing series was to evaluate thiosulfate effects on adipic acid consumption. Previous long-term material balance tests showed substantial losses of adipic acid in excess of that expected from scrubber solution removed with filter cake [12]. Laboratory experiments indicated that organic acid degradation is one of the major mechanisms of excessive adipic acid losses. It was suspected that adipic acid was decarboxylyzed into shorter chain organic acids, ethane, methane, and carbon dioxide by free radicals generated during oxidation of the SO_2 species [13]. Since sodium thiosulfate can inhibit oxidation and possibly deactivate those free radicals, it is likely that the adipic acid consumption can also be reduced by the presence of thiosulfate ions.

The adipic acid feed rate was maintained at 25 g/hr for the base case (run LA-0) and for run LA-2 with 500 ppm thiosulfate (Table 7). As the scrubber approached steady state, significant reduction in oxidation was obtained with sodium thiosulfate addition. However, the adipic acid concentration remained constant; i.e., there are no apparent effects of sodium thiosulfate on the adipic acid consumption rate. The data indicate that the mechanism of oxidation inhibition by thiosulfate may be different from that of adipic acid degradation. More data are required to identify the mechanism of each reaction.

An unexpected result obtained during this series of tests was the increase in SO_2 removal efficiency with thiosulfate addition. The SO_2 removal was 93% at 500 ppm $S_2O_3^{2-}$ (run LA-2), or 5% higher than the 88% in the base case (run LA-0). Although part of the increase is due to higher magnesium ion concentrations, the data suggest that there is no negative effect of sodium thiosulfate on the mass transfer enhancement by adipic acid.

Improvement in solids dewatering properties was observed when the thiosulfate ion concentration was raised to 2200 ppm (run LA-3). The hold tank slurry settling rate increased from 1.2 to 1.8 cm/min, and filter cake insoluble solids also increased from 52 to 59%. The synergistic effects of calcium chloride and thiosulfate were confirmed

by run LA-4. After the chloride ion concentration was raised to 7500 ppm, oxidation decreased to 0.9%, hold tank slurry settling rate reached 4.0 cm/min, and the filter cake insoluble solids increased to 69%.

CONCLUSIONS

The following conclusions are drawn from the pilot testing data:

1. Sodium thiosulfate is an effective additive for inhibiting sulfite oxidation. Both sulfate saturation and gypsum scaling were significantly reduced by $Na_2S_2O_3 \cdot 5H_2O$ addition in all five lime/limestone slurry FGD processes tested.
2. Deactivation of free radicals is the most likely oxidation inhibition mechanism of sodium thiosulfate. The concentrations of thiosulfate ion required to maintain unsaturated FGD operation and thus avoid gypsum scaling are 100 to 200 ppm. However, part of the thiosulfate added degrades or transforms into other sulfur species such as polythionates and accumulates in the scrubbing slurry.
3. In order to attain a sustainable thiosulfate concentration, the scrubber had to be spiked with doses of $Na_2S_2O_3 \cdot 5H_2O$ about 10 times higher than that required by a material balance. Pilot plant data indicate that, after the initial spiking, the normal consumption rate to achieve the oxidation inhibition effect should be in the range of 1 to 3 mmole $Na_2S_2O_3$/mole SO_2 absorbed for both the lime and limestone slurry FGD systems.
4. Sodium thiosulfate is an effective oxidation inhibitor in lime slurry scrubbers when the scrubbing liquor chloride ion concentration is below 300 ppm. When the HCl in flue gas caused high chloride ion concentration, thiosulfate addition could be less effective.
5. Improvement of solids dewatering properties was observed with the addition of sodium thiosulfate to both conventional and adipic-acid-enhanced limestone processes. Pilot plant data indicate that after the thiosulfate ion concentration reached 2000 ppm, both slurry settling rate and filter cake solids concentration increased. The effectiveness of thiosulfate on oxidation inhibition was enhanced by calcium chloride addition. However, thiosulfate accumulation had little effect on solids properties in the lime and magnesium-enhanced lime/limestone scrubbers.
6. The SO_2 removal efficiency of magnesium-enhanced lime/limestone scrubbers can be increased by thiosulfate addition through the decrease of sulfate saturation and increase of magnesium sulfite ion pair concentration.
7. No adverse effects of sodium thiosulfate addition on adipic-acid-enhanced limestone scrubbers were found. The SO_2 removal efficiency increased with the accumulation of thiosulfate in the pilot plant. Although oxidation was substantially reduced, no significant differences in adipic acid consumption rate were obtained between runs with and without thiosulfate.

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